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Abstract

The study of materials properties under extreme conditions has made considerable progress over the past decade due to both improvements in experimental techniques and advanced modeling methods. The availability of accurate models is crucial in order to analyze experimental results obtained in extreme conditions of pressure and temperature where experimental data can be scarce. Among theoretical models, *ab initio* simulations are playing an increasingly important role due to their ability to predict materials properties without the need for any experimental input. Ab initio simulations also allow for an exploration of materials properties in conditions that are unachievable using controlled experiments—such as e.g. the conditions prevailing in the core of large planets. In that limit, they constitute the only quantitative model of condensed matter available today. In this article, we review the current status of ab initio simulations and discuss examples of recent applications in which numerical simulations have provided an essential complement to experimental data.

Introduction

As high-performance computers are becoming more affordable, atomic-scale modeling is gaining importance as an investigation tool in materials science. Complementing micro- and meso-scale continuum models, atomic-scale simulations provide detailed information about dynamical and statistical properties of materials [1, 2]. Early simulations of solids and liquids were carried out in the 50s and 60s using simple model potentials. They were followed by calculations based on more realistic, interatomic potentials, usually derived to reproduce some known experimental data. Atomistic modeling of materials was mostly applied to normal thermodynamic conditions, where a large body of experimental data can be used to fit or constrain the models of interatomic interactions. When materials are subjected to high pressure and/or at high temperatures, the validity of most empirical models fitted to ambient conditions becomes questionable. Changing thermodynamic variables such as pressure and temperature can lead to phase transformations. Model parameters adjusted in one thermodynamic phase are likely to be inaccurate in a different phase. High temperatures also potentially lead to qualitative changes in chemical bonding, and corresponding changes in atomic coordination. The presence of multiple atomic species in alloys or molecular systems poses a particular challenge for the definition of accurate empirical interatomic potentials. Whereas a number of force fields have been parameterized for elemental substances,

parameterizations for binary compounds are rare. Such parameterizations can be obtained (as for e.g. biomolecular modeling) at the price of deriving environment-dependent potentials (i.e. potentials that depend on the species of neighboring atoms). This then restricts the use of such models to situations where chemical bonds remain fixed, i.e. cannot be broken or formed.

A successful theory of materials should be able to predict the microscopic structure of a material in arbitrary thermodynamic conditions. Furthermore, it should ideally provide information about electronic properties such as electrical conductivity or optical absorption. It was realized long ago that electronic structure determines the bonding properties of materials, and that any realistic description of structural properties of condensed matter should take into account electronic properties to some extent. Empirical quantum mechanical models have been proposed for specific materials, but suffer from the limited validity of their parameterizations when applied to extreme pressures and temperatures.

The development of Density Functional Theory [3, 4, 5] (DFT) during the past three decades has revolutionized the field of atomistic simulation. This advance was due to a number of groundbreaking contributions starting with the framework of the Kohn-Sham equations [4], and the appearance of the first ab initio calculations of the exchange-correlation energy of the electron gas by Cerperley and Alder [6], which provided a practical way of solving the Kohn-Sham equations without any empirical input. Following numerous developments that we briefly review in the next section, ab initio simulations have now become reliable enough to play an important role in investigations of materials subjected to extreme conditions.

It should be noted that DFT calculations do not by far constitute the only ab initio model of electronic structure. Other approaches based on Quantum Chemistry, many-body perturbation theory, and the Quantum Monte Carlo (QMC) method [7] share the property of predictive first-principles simulations. However, DFT appears to strike the right balance between accuracy and computational complexity. This last quality was a key factor in the large impact that DFT simulations have had on materials science in the past two decades.

Ab initio calculations

Among the early applications of Density Functional Theory was the calculation of the band structure of periodic solids, which allowed for the interpretation of various spectroscopic experiments. It was followed by the computation of the energy of solids demonstrated as early as 1979 by Ihm et al [8]. Shortly thereafter, the pioneering calculations by Yin and Cohen [9], in which the equation of state of semiconductors was first explored from first principles, marked the beginning of ab initio static computations of structural properties of solids under pressure. The success of this approach was such that it was dubbed the “standard model of condensed matter” in reference to the famous Standard Model unifying the electro-weak interactions of high-energy physics, developed a decade earlier.

At that point, physicists were able to study the equation of state through series of static calculations in which internal parameters of a crystalline structure were optimized, given a fixed unit cell. This was limited to known structures, of high symmetry. It allowed one to evaluate the relative phase stability of various phases of simple solids. Dynamical effects were sometimes taken into account using linear models including entropic

contributions derived from computed phonon spectra in the harmonic approximation. This approach remains a very useful approach to the computation of free energies in situations where crystal structures are known. In the early 80's, other quantities, such as the melting temperature, were not yet accessible by ab initio calculations. Furthermore, the optimization of complex systems, i.e. systems containing multiple species and many atoms in their primitive cells, remained difficult.

An important breakthrough took place in 1985 when Car and Parrinello introduced a unified approach to combine molecular dynamics with DFT [10] thus giving access to finite-temperature quantities. Within this approach, ab initio computations could include entropic and anharmonic effects, and calculations of free energies were not limited by linear approximations of the phonon spectrum. The combination of DFT and MD provided a unique ability to study the formation and breaking of chemical bonds. This new feature could lead to the discovery of unexpected behavior of materials.

A distinct advantage of the Car-Parrinello approach was the consistent and simultaneous computation of electronic, structural and dynamical properties: this was essential for the interpretation of experiments measuring electronic properties (e.g. conductivity in a high-pressure shock experiment) but providing no information about structural properties. An obvious drawback of the approach is its computational cost, which limits the amount of physical time that can be simulated in a calculation. The Car-Parrinello approach has been applied successfully to many areas including solid-state physics, the theory of liquids, biochemistry and more recently nanotechnology. After a number of technical developments that took place in the early 90's, the Car-Parrinello method came to revolutionize the field of high-pressure modeling and achieved sufficient accuracy to yield results comparable to experiments.

Implementing ab initio molecular dynamics

Implementing the ab initio molecular dynamics method consists in solving the Kohn-Sham (KS) equations describing the electronic structure at each time step of a molecular dynamics simulation. Solutions are then used to compute forces acting on the atomic nuclei. These forces are in turn used to compute the positions of nuclei at the next time step of the molecular dynamics simulation.

A wide variety of numerical methods have been developed to solve the KS equations, and we can only give a brief summary of the main steps involved here. We refer to the textbook of Martin [11] for an in-depth treatment of the subject.

The KS equations are a set of non-linear integro-differential partial differential equations for the one-particle wavefunctions $\phi(\mathbf{r})$ describing each electron.

$$\begin{cases} -\Delta\varphi_i + V(\rho,\mathbf{r})\varphi_i = \varepsilon_i\varphi_i \quad i = 1\ldots N_{\text{el}} \\ V(\rho,\mathbf{r}) = V_{\text{ion}}(\mathbf{r}) + \int \dfrac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + V_{\text{XC}}(\rho(\mathbf{r}),\nabla\rho(\mathbf{r})) \\ \rho(\mathbf{r}) = \sum_{i=1}^{N_{\text{el}}} |\varphi_i(\mathbf{r})|^2 \\ \int \varphi_i^*(\mathbf{r})\,\varphi_j(\mathbf{r})\,d\mathbf{r} = \delta_{ij} \end{cases} \tag{1}$$

They have the structure of a set of one-particle Schrodinger equations for independent electrons placed in an effective potential $V(\rho,r)$ describing the electron-ion and the electron-electron interactions. The effective potential includes an electrostatic potential $V_H(r)$ generated by the electron density $\rho(r)$, and an exchange-correlation term V_{xc} which depends in a complicated way on the electron density. The choice of an approximate density functional determines the functional form of $V_{xc}(\rho,r)$. In most implementations, the solutions of the KS equations must be kept orthogonal, which entails a large computational cost that grows asymptotically as $O(N^3)$ for N electrons. The numerical solution of the KS equations usually relies on a discretization based on the projection of the solutions on a set of basis functions. This discretization leads to an algebraic eigenvalue problem that must be solved repeatedly until the electronic charge density $\rho(r)$ derived from the solutions (as defined in Eq. (1)) is consistent with the input density. Practical calculations of materials properties under pressure were made possible by a number of technical advances. Reliable calculations of the stress in a solid followed the work of Nielsen and Martin [12] who provided the necessary framework. The variable cell molecular dynamics method originally proposed by Parrinello and Rahman [13] was extended to ab initio simulations by Wentzcovitch et al. [14] who used it to perform constant-pressure ab initio simulations. Focher et al. [15, 16] proposed a method to perform DFT electronic structure calculations with constant resolution in variable-sized simulation cells. This new technique was then used to perform numerous constant-pressure ab initio simulations [17, 18]. Continuing progress in the development of accurate pseudopotentials was an essential contribution to ab initio MD simulations [19, 20]. The development of efficient methods for using non-local pseudopotentials were also instrumental [21] in extending the size of feasible simulations. Finally, an important contribution that made ab initio simulations a reality is the continuing increase in available computing power that took place during the past two decades. As high-performance parallel clusters have become more common, all modern software implementations of ab initio MD have adapted to this type of resource, and are now based on parallel codes.

Examples of applications

Ab initio simulations have been used in numerous investigations of materials subjected to extreme conditions. Examples of applications include calculations of the equation of state of elemental solids such as hydrogen [22, 23, 24, 25], boron [26, 27], carbon [17, 28, 29], aluminum [30], semiconductors [31], oxides [14, 32], silica [33, 34], iron [35], and other transition metals [36, 37]. Ab initio simulations have found particularly fruitful applications in geophysics [38], where they have provided new insight into the equation of state of iron [39, 40, 41, 42] and perovskites [43, 44, 45] in the conditions of the Earth's core. Ab initio calculations have also been used in the search for artificial ultra-hard materials that could rival or surpass diamond on the hardness scale [46].

Rather than attempting to give an exhaustive overview of applications, we discuss a few selected examples of recent uses of ab initio simulations. We focus on the problem of structure determination at high pressure, investigations of chemical reactions in extreme conditions and the calculation of melting temperatures.

Structure identification

The search for new crystalline phases of solids at high pressure has recently made rapid progress through the development of experimental techniques [47], including diamond anvil cells (DACs) and the use of synchrotron radiation. Typical high-pressure experiments consist in compressing small samples of materials in the DAC while measuring diffraction patterns formed by X-ray beams going through the samples. Most often, the crystals formed in a high-pressure phase are polycrystalline, i.e. they consist of a multitude of microcrystalline domains having random orientations. Due to this orientational disorder, the observed X-ray diffraction patterns are similar to powder diffraction patterns, and thus provide only limited information about the crystal structure. The exact crystal symmetry, in particular the crystallographic space group, is not completely determined by such an experiment. Faced with this situation, scientists must examine all possible crystal structures that are compatible with the observed X-ray diffraction pattern and retain only the ones that best match the diffraction data. This search for appropriate crystal space groups can be daunting. Some candidate structures can often be ruled out because they involve unrealistic interatomic distances. However, multiple candidate structures are sometimes retained on the basis of their fit to diffraction. Ab initio simulations provide extremely useful assistance in this search process since they provide a test that discriminates structures on the basis of their energetics and their thermodynamic stability. Candidate crystallographic structures are used as input for ab initio simulations in which internal coordinates (i.e. atomic positions) are relaxed in order to minimize energy. In situations where the structure is unfavorable, the simulation almost always relaxes immediately toward a different structure, indicating that the initial guess is not a good candidate. If the structure is found to be (locally) stable, it can be tested for possible metastability by performing molecular dynamics simulations at high temperature. Finally, when a satisfactory structure is identified, an ab initio calculation of the corresponding external stress can be used to confirm that the stress is isotropic, and that it indeed corresponds to the pressure at which the experiment was carried out. This procedure can be repeated for each candidate structure. It should be noted that a naïve approach consisting in simulating a liquid under pressure and letting it cool until it crystallizes is not a viable option. The solidification process is known to depend strongly on interatomic correlations in small simulation cells, and such a simulation procedure usually leads to the formation of an amorphous phase whose energy is higher than the "optimal" crystalline phase.

Recently, ab initio simulations were used to help identify new high-pressure phases of CO_2 . Diamond anvil cell experiments [48] led to the observation of a new three-dimensional polymeric crystalline phase of CO_2 at high pressure. The exact structure of the new phase was not determined although clear evidence was found that it was not a molecular phase. This situation was challenging for any empirical model, since the bonding character of CO_2 changes during the transformation from an assembly of weakly interacting molecules to a strongly bonded, covalent network.. Simple models of intermolecular interactions had been used in the past to describe molecular phases [49], but were not likely to describe a polymeric phase accurately. Ab initio simulations were used to examine a number of candidate phases inspired from the phase diagram of SiO_2 [48], identifying a tridymite phase [50] (space group $P2_12_12_1$) as the best structure reproducing the observed diffraction features in the experimentally observed unit cell. The high

pressure phases of CO_2 were further investigated by Holm et al [51] and Dong et al. [52] using static ab initio calculations. Ab initio simulations were also used to investigate the stability of low-pressure phases of molecular CO_2 solids [53].

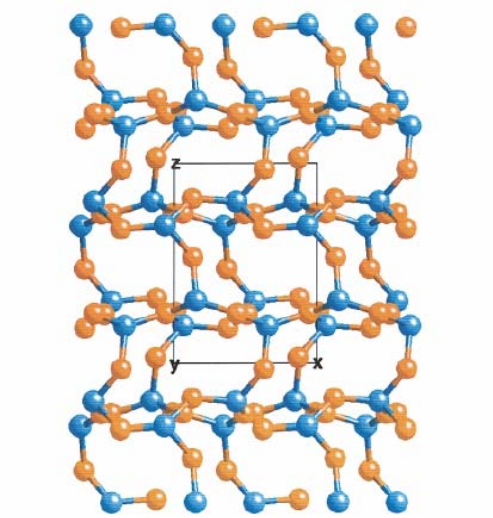

Figure 1. Structure of polymeric carbon dioxide (CO_2-V) observed in high-pressure experiments. This structure, similar to known tridymite phases of silica, was proposed on the basis of ab initio calculations of the enthalpy of several candidate structures [48].

Chemical reactions at high pressure

Beyond the study of equilibrium structural properties, ab initio simulations can be used to investigate processes occurring far from equilibrium. For example, the unique capability of ab initio simulations to describe the formation and breaking of chemical bonds makes them well suited for studies of chemical reactions in hot dense liquids. Recently, Manaa et al. [54]. carried out ab initio molecular dynamics simulations of the decomposition of nitromethane at high pressure and high temperature. They considered conditions similar to those encountered during detonation and concluded that the first step in the decomposition process is an intermolecular proton abstraction reaction. These simulations provided direct evidence of various chemical species appearing (and disappearing) during the early stages of the decomposition, including the eventual formation of water as a stable product. Note that the extreme conditions present in this situation turn out to be an advantage, and make it possible to readily observe chemical reactions taking place over less than a picosecond. Chemical reactions occurring in the gas phase or in the liquid in normal conditions can be much more difficult to observe directly, since they occur very rarely on the time scales that are accessible by simulation.

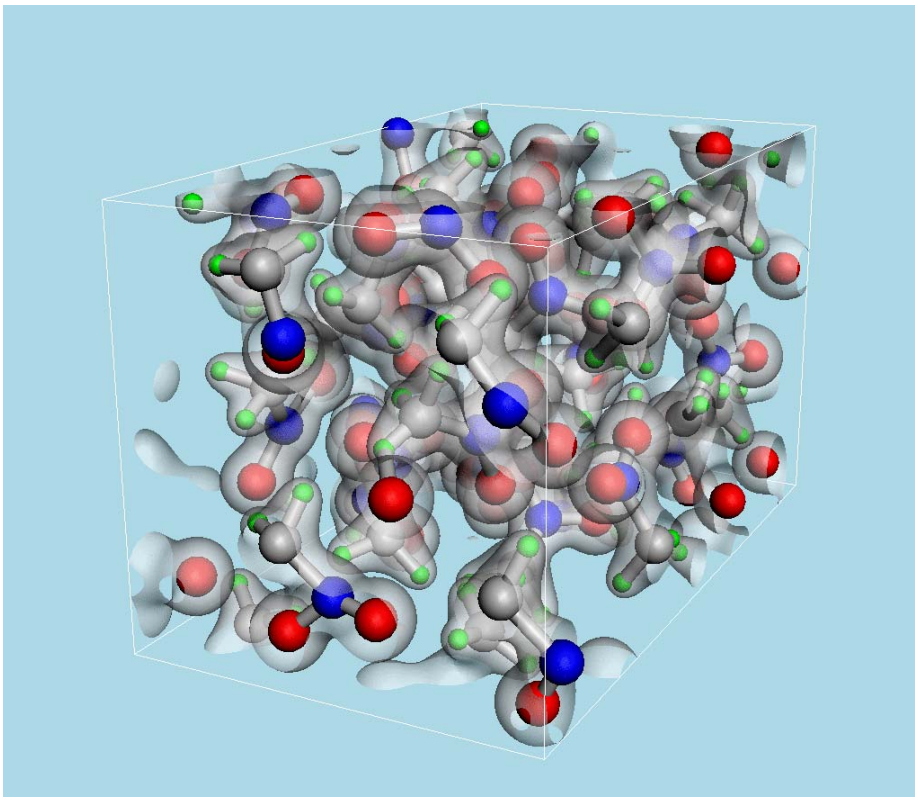

Figure 2. Ab initio simulation of hot dense nitromethane [54]. Colored spheres represent the positions of atoms (oxygen in red, carbon in grey, nitrogen in blue and hydrogen in green) in a snapshot of a simulation performed at 4000 K. The electronic charge density is represented as a white isosurface. This simulation reveals the mechanisms of chemical reactions occurring in extreme conditions in the condensed phase.

Computing melting temperatures

Several methods have been developed to explore the phase diagram of a substance using molecular simulations [2]. Among them, thermodynamic integration [55] is a simulation technique that allows for the computation of free energy variations when a given system is subjected to varying thermodynamic conditions. This approach can be used to locate phase boundaries in the phase diagram of a substance, e.g. the boundary separating a solid phase from the liquid phase (the melting line), or the boundary between two solid phases of different lattice symmetry [56]. It was first used in the context of ab initio simulations by Sugino and Car to compute the melting temperature of silicon in normal conditions [57]. This approach has been extended to high pressure simulations and recently, Vocadlo and Alfe computed the melting temperature of fcc aluminum up to a pressure of 150 GPa [30]. In this case, the free energy of the solid phase was computed within a quasiharmonic approximation, and the free energy of the liquid was obtained via thermodynamic integration from a series of separate ab initio molecular dynamics simulations.

More recently, Ogitsu et al. used the two-phase simulation method [32] applied to ab initio molecular dynamics to locate the melting temperature of lithium hydride at high pressure

[58]. In the two-phase simulation method, one computes molecular dynamics trajectories of a sample made of two regions: one part solid and one part liquid, placed in contact. Simulations are performed at constant pressure *P* and temperature *T*. If the *(P,T)* conditions are such that the equilibrium phase is a solid, the sample gradually transforms into a solid during the simulation, i.e. the solid region grows and the liquid region disappears. Conversely, if the conditions are those favoring a liquid phase, the liquid phase will eventually fill the entire simulation cell. When used repeatedly with different temperatures, this technique allows one to locate the melting point for any given pressure, and thus the melting line in the *(P,T)* phase diagram. The same method was used to compute the melting line in hydrogen [25] and aluminum [30].

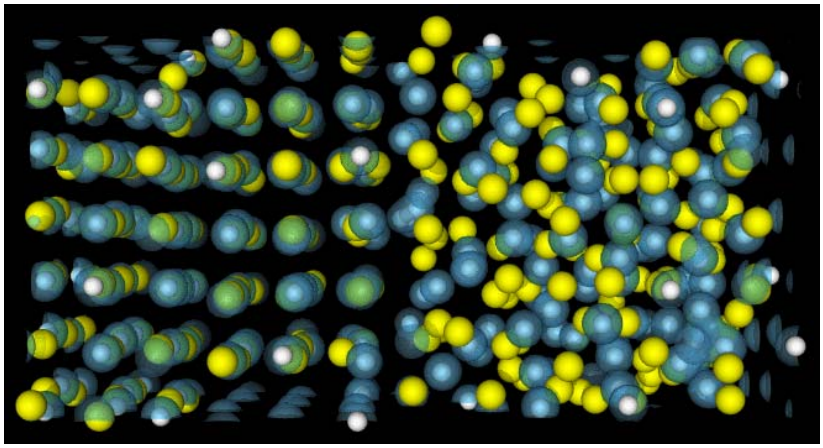

Figure 3. Snapshot of an ab initio two-phase calculation of the melting temperature in LiH. The Li and H atoms are represented by yellow and white spheres respectively. The electronic charge density is represented by a blue isosurface. The solid region (ordered) is located in the left half of the simulation cell, and the liquid region (disordered) in the right half. This simulation [58] provided predictions of the melting temperature at high pressure.

Current challenges and future directions

Ab initio simulations are rapidly gaining importance as a tool complementing experimental investigations. Continuing progress in the development of more accurate density functionals [59], as well as more efficient numerical algorithms for the solution of the Kohn-Sham equations contribute to improving the size and accuracy of feasible simulations. We conclude by briefly mentioning a few areas where improvements are most needed for ab initio simulations to tackle more challenging problems of materials science.

Ab initio molecular simulations are affected by the same restrictions that limit classical molecular dynamics [60]: some dynamical processes that occur over long time scales cannot be captured by molecular simulations having limited durations. This limitation is even more severe in the ab initio case, in which the computational cost per time step is orders of magnitude larger than in the classical case.

Furthermore, since the vast majority of ab initio simulations are based on the use of the Kohn-Sham equations, they suffer from all the known drawbacks of currently available density functionals. In particular, systems in which intermolecular interactions are weak (e.g. dominated by van der Waals interactions) are not well described by local density functionals. This problem is however not seriously affecting high-pressure simulations, in which intermolecular interactions are often dominated by strong repulsive interactions. All currently known density functionals are unable to predict correctly the magnitude of a band gap in the one-particle excitation spectrum—although general trends are often properly described. This has the consequence that ab initio simulations cannot currently predict accurately the pressure at which an insulator turns into a metal. More elaborate electronic structure methods are needed to overcome this difficulty. Considerable progress has recently been made to make the Quantum Monte Carlo method a competitive electronic structure method. It was used by Ogitsu et al. [58] to refine the result of their calculation of the melting point of LiH, by Hood and Galli in calculations of the electronic structure of hydrogen [61], and more recently in a study of the rocksalt to CsCl phase transition in MgO [62]. QMC calculations are typically carried out using static atomic configurations extracted from MD simulations, although a promising approach to combine QMC and MD has recently been proposed [63].
DFT also has known deficiencies in the description of systems in which strongly correlated electrons play an important role. This limits its validity for systems such as transition metals and actinides. In situations where electron correlations are important, more accurate models of electron-electron interactions such as the dynamical mean-field method [64] (DMF) have been proposed and combined with DFT [65]. For example, Savrasov et al. [66] applied the DMF approach to compute the electronic structure of δ-Pu.
These areas are all subjects of active research. Progress in these directions will likely further enhance the usefulness of ab initio simulations in materials science.

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